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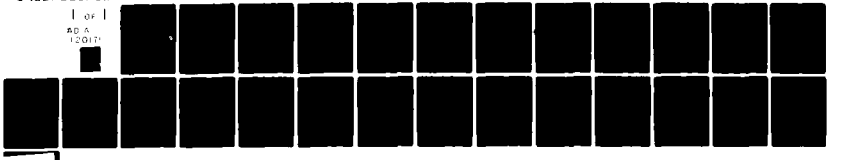

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Mapping the Efficiency of Electron-Hole Pair Separation for a Semiconductor Electrode. Luminescent Properties of Graded Cadmium Sulfoselenide Electrodes.

by

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Inhomogeneous samples of n-type CdS_XSe_{1-X} ($0 \leq X \leq 1$) have been prepared by vapor-phase diffusion of S into a single-crystal CdSe substrate. Characterization by Auger electron spectroscopy (AES) in conjunction with Ar ion sputter etching reveals that S has substituted for Se in the lattice to produce a graded region. The depth profile analysis indicates a composition of CdS over the first ~0.05 μm from the surface; over the next ~2 μm from the surface, the composition monotonically decreases in X, corresponding to a

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decline in band gap energy from ~2.4 eV for CdS to ~1.7 eV for CdSe. Photoluminescence (PL) and electroluminescence (EL) from the graded material appear to derive from the luminescence of the CdS_xSe_{1-x} compositions which comprise the graded region: Emission from ~470-750 nm matches the spectral region spanned by PL and EL from homogeneous, single-crystal $CdS_xSe_{(1-x)}$ samples which emit near their band gap energies. This assignment is also supported by chemical etching experiments in which the removal of S-rich, near-surface strata progressively red-shifts the PL spectrum. A previously established linear correlation between emission maxima (nm) and composition in homogeneous CdS_xSe_{1-x} samples provides a spatial probe of electron-hole (e^- - h^+) pair recombination in the inhomogeneous material: Regions from which PL and EL originate can be inferred from their spectral distribution in combination with the AES/depth profile data. PL spectra are thus shown to be dependent on excitation wavelength in a manner consistent with relative optical penetration depth, and EL is shown to originate, on average, from nearer the semiconductor surface than PL from ultraband gap 457.9-nm excitation. The inhomogeneous samples can be used as photoanodes of photoelectrochemical cells employing aqueous (poly)sulfide electrolyte. The photoaction spectrum exhibits an onset at ~550 nm, indicating that the S-rich, near-surface region is principally responsible for photocurrent. This spatial origin is also reflected in the nonuniform quenching of PL accompanying passage of photocurrent from 457.9-nm excitation: With certain assumptions, the PL quenching properties provide a map relating the efficiency of e^- - h^+ pair separation to distance from the semiconductor-electrolyte interface. For this material, efficient separation obtains within ~0.4 μm from the surface.

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The depletion region of semiconductor electrodes plays a critical role in photoelectrochemical cells (PECs) in that the electric field which defines the region efficiently separates electron-hole (e^--h^+) pairs to produce photocurrent.[1] Competing with this mode of excited-state decay are the radiative and nonradiative recombination of e^- - h^+ pairs. Among the luminescent systems we have used to examine recombination processes in PECs are solid solutions of n-type, single-crystal CdS_XSe_{1-X} $(0 \leq X \leq 1)$[2] for which the band gaps increase monotonically with X from ∿1.7 eV for CdSe to ∿2.4 eV for CdS.[3] The homogeneous CdS_XSe_{1-X} samples exhibit both photoluminescence (PL) and electroluminescence (EL) near their band gap energies; noteworthy features of these spectra are their sharpness (fwhm of ∿0.05-0.08 eV) and nearly linear shift in λ_{max} with composition, eq. (1).[2,4]

$$\lambda_{max}(nm) \cong 718 - 210\ X \qquad (1)$$

While conducting these studies, it occurred to us that spatially inhomogeneous CdS_XSe_{1-X} samples might provide a means, in conjunction with eq. (1), for probing spatial aspects of recombination. In this paper we describe the luminescent features of one such system containing a graded region. We demonstrate for this material that its color-coded luminescence permits the regions from which EL and PL originate to be inferred from their spectra. Moreover, when the sample is used as a PEC electrode, its PL properties may, with certain assumptions, be interpreted in terms of a map which correlates the efficiency of e^- - h^+ pair separation with distance from the semiconductor-electrolyte interface.

Results and Discussion. Sections below describe the synthesis and composition of the inhomogeneous samples of this study, their PL and EL properties, and the perturbation of their PL features in a PEC. The luminescence of homogeneous CdS_XSe_{1-X} samples provides a framework in which to interpret emissive properties of the graded samples and is discussed, as well.

A. Synthesis and Composition. Previous studies have established that CdS_XSe_{1-X} samples may be prepared by the vapor-phase diffusion of S into CdSe or of Se into CdS; homogeneous, mixed samples were obtained in long-term exchange reactions, whereas graded materials resulted from short-term experiments.[5-12] Neutral interstitial chalcogens have been proposed as the diffusing defect.[6] Our synthesis of inhomogeneous CdS_XSe_{1-X} samples is based on the vapor-phase technique and involves the short-term diffusion of S into an etched, single-crystal CdSe substrate. Typically, CdSe was heated in an evacuated quartz ampule at 700°C for 1 hr, first in the presence of S and then in the presence of Cd.[13]

The composition of the solid was determined by Auger electron spectroscopy (AES): A depth profile was obtained by sputter etching with Ar ions at a rate of ∿300 Å/min, while monitoring the AES signals of Cd, S, and Se. Figure 1 shows that for the first ∿500 Å (0.05 μm) only Cd and S are observed. Over the next ∿2 μm from the surface are sulfoselenide compositions which monotonically decrease in X until only the Cd and Se signals of the substrate are seen. Of course, S may still be present at this depth and beyond, but at concentrations too low to be detected by AES.

Two features of the AES/sputter data provide strong evidence that S is predominantly substituting for Se in the lattice rather than occupying interstitial sites. First, the absence of a Se signal over a distance of ∿500Å from the surface indicates that the Se contribution to the material composition in this region is minor, at best.

Second, at any of the sputter times of Fig. 1, the fractional S and Se compositions total to roughly unity when each is expressed as a fraction of its maximum AES signal. Additional support for lattice substitution comes from luminescence and photoaction data (vide infra).

The distances extracted from Figure 1 will be used to interpret luminescence properties and merit further comment. Because S can be driven towards the bulk by the sputtering process, these distances should be regarded as upper limits.[14] To verify that they are roughly correct, however, we made use of the change in PL properties accompanying conversion of the substrate to the graded sample: One-half of such a sample was masked and the exposed portion was chemically etched until its PL spectrum began to exhibit features characteristic of the substrate. After removal of the mask, a contacting stylus was passed over the step and indicated its height to be ∿1.0 μm. An analogous experiment in which etching was continued until only the substrate PL spectrum was observed corresponded to a step height of ∿1.8 μm.

Two other sample characteristics of interest are electrical conductivity and the degree of crystallinity of the graded region. One measure of conductivity is the sample's ability to serve as a PEC electrode. Although the CdSe substrate satisfied this criterion, the S-treated material did not, and necessitated the heat treatment with Cd to restore this capability. Despite their worthiness as electrodes, however, the inhomogeneous samples gave evidence of possessing a resistive layer in resistivity and capacitance measurements. In the former case, no reliable reading could be obtained in a four-point probe experiment. The capacitance of the exchanged material, measured at 1 MHz at several depths in the graded region, gave values which were independent of applied voltage (0-20 V) and ranged from 180 pF near the surface to 20 pF near the substrate; in contrast, the substrate exhibited the expected Schottky-Mott behavior.[1a,b]

We found the degree of crystallinity of the graded samples difficult to assess directly. Preservation of crystallinity is implicit in much of the previous work which examined absorption and emissive features of related, graded samples and, in some cases, their use as optical waveguides.[5-12] To examine this question under our preparative conditions, we ran a long-term exchange experiment in which we sought to convert crystalline CdSe powder to CdS. After 4 days at 700°C, an X-ray powder pattern was taken and confirmed the presence of crystalline CdS. Although this does not prove the retention of crystallinity under our short-term conditions, it does suggest that some degree of crystallinity is likely, a conclusion supported by the luminescence data described below.

B. PL and EL properties. Luminescence measurements corroborate the sample composition inferred from the AES data. Curve 1 of Figure 2 displays a PL spectrum, obtained in air with 457.9-nm excitation, of an as-grown sample. The presence of emission at $\lambda \lesssim 700$ nm is consistent with the lattice substitution of S for Se for two reasons. First, preservation of the CdSe lattice (interstitial S) would make this ultraband gap emission, an extremely unlikely process. Second, the PL spectrum spans ~470-750 nm, wavelengths consistent with emissive contributions from various single-crystal CdS_xSe_{1-x} compositions, as given by eq. (1). Representative PL spectra of several homogeneous CdS_xSe_{1-x} samples taken under similar conditions are shown in Figure 3; these spectra are well-fit by eq. (1).[2b,c,4]

That the PL of these graded samples is a composite of PL spectra of the homogeneous mixed samples is most convincingly demonstrated by chemical etching. Curves 2-5 of Figure 2 correspond to PL spectra taken under nearly identical excitation conditions after successive etchings of the graded sample. Although the likelihood of nonuniform etching precludes a quantitative analysis,[7] the progressive red-shift of λ_{max} and of the short-wavelength PL onset is consistent with the loss of near-surface, S-rich compositions as etching proceeds. Ultimately, the PL spectrum approaches that of the CdSe substrate, curve 5 in Figures 2 and 3. Similar etching effects on these systems have been reported for PL spectra taken

at 77 K.[7] It is important to note that although the PL spectra appear to be dominated by the edge emission of CdS_xSe_{1-x} compositions, we cannot rigorously exclude small spectral contributions from impurities, e.g. Even in this case, however, the states involved in subband gap transitions would need to lie relatively near the band edges, since we only observe emission between ∿470-750 nm; no PL signal was observed from 750-1100 nm. We should mention, too, that we do see modest variations in the PL spectra of different samples, perhaps reflecting slight differences in growth conditions.

Different means of producing luminescence in the S-exchanged sample also support the sample inhomogeneity inferred from the AES data: Figure 4 reveals that four different modes of excited-state population result in four different emission spectra. The three PL spectra of Figure 4 were obtained with equal intensities of 457.9-, 514.5-, and 580-nm excitation. Because only 457.9-nm light exceeds the band gaps of all CdS_xSe_{1-x} compositions, it should have the shortest penetration depth, followed, in turn, by 514.5- and 580-nm light which require successively more Se-rich compositions to be strongly absorbed; we estimate the absorptivity, α, for 457.9-nm light to be $\sim 10^5$ cm^{-1} for all sulfoselenide compositions, whereas α for CdS is $\sim 10^2$-10^3 cm^{-1} at 514.5 nm and negligible by 580 nm.[3d,f] Consistent with this ordering, the longer excitation wavelengths do yield PL spectra with greater contributions from the deeper, more Se-rich compositions. Quantifying these contributions awaits investigation of the relative emissive efficiencies of the various CdS_xSe_{1-x} compositions, self-absorption effects, and of the roles of e^- - h^+ ambipolar diffusion and excited-state energy transfer processes.

That e^- - h^+ ambipolar diffusion and/or excited-state energy transfer processes may be important in the graded material is intimated by the PL spectra produced by 457.9-nm excitation, Figs. 2 (curve 1) and 4. From the AES data and 457.9-nm absorptivity, this wavelength should not penetrate much beyond the CdS layer, yet emission from relatively Se-rich compositions is observed. This observation

suggests that the aforementioned processes might involve distances on the order of a micron. Similar effects were reported based on 77 K PL spectra of related, graded CdS_XSe_{1-X} samples with the spectral broadening exploited to estimate diffusion lengths.[7] An alternative explanation for the broad PL spectra from 457.9-nm excitation is lateral inhomogeneity. The presence of CdSe "pinholes", for example, could introduce low-energy PL contributions. We probed this possibility by focusing the Ar ion laser beam to a diameter of ∿0.5 mm and comparing the PL spectra resulting from excitation at a number of sites on the crystal surface. Reproducibility was generally quite good, variations in the spectral distribution being ≤15% over 6 sites. Although this observation suggests that gross lateral inhomogeneities are absent, some inhomogeneity may well be present and should be kept in mind, since it could influence the results described below.

Also pictured in Fig. 4 is an EL spectrum obtained in $OH^-/S_2O_8^{2-}$ electrolyte using a technique in which the semiconductor electrode is repetitively pulsed between 0.00 V and a potential sufficiently cathodic to initiate reduction of $S_2O_8^{2-}$; the mechanism by which EL is proposed to proceed involves reduction of $S_2O_8^{2-}$ to $SO_4^{\cdot-}$ which then injects a hole into the valence band to populate the emissive excited state.[15] We found the EL spectral distribution of Fig. 4 to be independent of the cathodic potential employed for potentials between ∿-1.2 to -1.5 V vs. SCE. The salient feature of the EL spectrum is its blue-shifted position relative to the 457.9-nm PL spectrum. This indicates for this material that EL originates, on average, nearer to the semiconductor-electrolyte interface than PL from 457.9-nm excitation, a conclusion also drawn for homogeneous CdS_XSe_{1-X} samples from self-absorption effects.[2] Moreover, from eq. (1), Figure 1, and the onset of EL at ∿630 nm, we deduce that EL occurs within ∿0.5 μm of the electrode surface.

C. PL Properties in a PEC. The graded samples of this study have been investigated as electrodes in PECs employing aqueous sulfide (1M OH^-/1M S^{2-}) or polysulfide (1M OH^-/1M S^{2-}/0.1M S) electrolyte. Figure 5 presents a plot of relative photocurrent vs. excitation wavelength in transparent sulfide electrolyte with the electrode at -0.30 V vs.SCE. The principal response in this photoaction spectrum onsets at ∿550 nm, again confirming the predominantly substitutional rather than interstitial incorporation of S. Overall, the photoaction spectrum resembles that of CdS[16] and indicates that the S-rich, near-surface compositions of the material are primarily responsible for photocurrent.

As the photoanode of a PEC employing polysulfide electrolyte, the inhomogeneous solid yields reasonable i-V properties upon 457.9-nm excitation.[17] The inset of Figure 6 presents a typical i-V curve, corresponding to a maximum monochromatic energy conversion efficiency of 3.7% and a photocurrent quantum efficiency, ϕ_x, of 0.37 at -0.30 V vs. SCE. Most remarkable, however, is the contrast between open-circuit and in-circuit PL spectra, the latter pictured in Figure 6 at -0.30 V vs. SCE. Unlike homogeneous CdS_xSe_{1-x} samples where only the PL intensity is perturbed by the passage of anodic photocurrent, Figure 6 demonstrates that the PL spectral distribution of the inhomogeneous sample is potential-dependent. In particular, the intensity of the high-energy portion of the PL band, corresponding to contributions from S-rich, near-surface regions, suffers quenching of up to ∿50% between open circuit and -0.30 V vs. SCE; by comparison, no quenching is found in the low-energy PL tail which corresponds to contributions from the more remote, Se-rich regions. Such nonuniform quenching may be useful in display technology.

We have constructed a simple model to account for the Figure 6 data using eq. (2) which relates the open-circuit and in-circuit radiative efficiencies (ϕ_{r_o} and ϕ_{r_i}, respectively) to ϕ_x. This relationship, based on the assumption

$$\frac{\phi_{r_o}}{\phi_{r_i}} = \frac{1}{1 - \phi_x} \tag{2}$$

that the ratio of radiatively to nonradiatively recombining $e^- - h^+$ pairs is unaffected by potential, is roughly obeyed for monochromatic excitation by homogeneous CdS_xSe_{1-x} samples.[2] The relationship has also been satisfied at various potentials and incident intensities with homogeneous Te-doped CdS (CdS:Te) electrodes and with homogeneous doped and undoped ZnO electrodes.[1 0] In essence, eq. (2) states that the fraction of $e^- - h^+$ pairs diverted to photocurrent is the fraction by which the PL intensity is quenched. For a homogeneous emissive electrode we presumably see a spatially weighted average, since the efficiency of $e^- - h^+$ pair separation should decrease with distance from the interface as band bending diminishes. For the inhomogeneous system the same logic suggests that the fractional quenching observed at the different PL wavelengths corresponds to the efficiency of $e^- - h^+$ pair separation from the composition and region associated with that wavelength. Thus, the use of eqns. (1) and (2) in conjunction with Figures 1 and 6 provides a crude map of the efficiency of $e^- - h^+$ pair separation as a function of distance from the semiconductor-electrolyte interface. Our data then indicate, for example, that in the first ∿0.1 μm from the surface ∿30-50% of the $e^- - h^+$ pairs separate to produce photocurrent, whereas by ∿0.4 μm from the surface negligible separation obtains. This spatial dependence is in rough accord with that deduced from the photoaction data of Figure 5.

Although appealing in its simplicity, the construction of the aforementioned map hinges on several assumptions relating to material properties. In particular, we are assuming the exclusive presence of edge

emission in PL spectra, lateral homogeneity, and the accuracy of distances extracted from Fig. 1. We also assume the validity of eq. (2), i.e., that the ratio of radiatively to nonradiatively recombining $e^- - h^+$ pairs in the material is independent of electrode potential over the potential regime examined. It is worth pointing out, in fact, that even homogeneous electrodes exhibit discrepancies from eq. (2) for reasons we do not fully understand but which may involve such phenomena as surface states and electroabsorption effects.[18a]

Another description of the spatial correlation deduced from the PL quenching results is as a map of the effective electric field in the graded sample. For a homogeneous semiconductor this could be described simply as a map of the depletion region. However, the electric field present in the graded system can be considerably more complex: besides possessing space-charge and applied-voltage contributions, it may also contain terms based on band-edge and effective-mass gradients, hence its description as an effective electric field.[21] Although a detailed description of these effects is premature at present, we do note that the electronic structure of related systems has been discussed in connection with exchange reactions involving a CdSe electrode in a PEC employing polysulfide electrolyte.[22,23] The band diagrams proposed for a composition with CdS on CdSe predict the presence of a barrier in the valence band which would block the passage of holes to the surface; a conduction band barrier blocking passage of electrons into the bulk may also be present. The existence of such barriers in the graded region might well account for our results; we do, in fact, see a decline in $e^- - h^+$ pair separation efficiency over a proportionately shorter distance when the graded region is only $\sim$1 μm thick.[13] A better understanding of the electronic structure of these systems should emerge from examination of additional graded materials, studies which are in progress. At this point, however, we feel that the studies described herein amply demonstrate the viability of using inhomogeneous luminescent semiconductor electrodes to probe spatial features of $e^- - h^+$ pair recombination relevant to PECs.

Experimental Section

Materials. Graded CdS_xSe_{1-x} samples were prepared from ∿5x5x1-mm, vapor-grown, single-crystal c plates of n-CdSe (resistivity ∿2 ohm-cm; four-point probe method), obtained from Cleveland Crystals, Inc., Cleveland, Ohio. In a typical procedure, a CdSe plate was etched in Br_2/MeOH (1:10 v/v) and placed in a 6-mm i.d., 8-mm o.d. quartz tube (William A. Sales, Ltd., Wheeling, Ill.) with ∿1 mg of S; the S was purchased from Alfa Products, Danvers, Mass. and was free of metallic impurities to better than 10 ppm. The quartz ampule was evacuated (∿1 torr), sealed to a volume of ∿2 cm^3, and placed in a preheated Lindberg furnace (700°C) for 1 hr. After the ampule was removed from the furnace, one end was contacted by a heat sink to prevent the S from condensing on the crystal. The crystal was then removed, placed in a similar tube with ∿1 mg of Cd, evacuated and sealed, and again heated at 700°C for 1 hr; the Cd was obtained from Alfa and had ≤1 ppm of metallic impurities. After its removal from the ampule, the crystal was mounted as an electrode as described previously.[18b] The preparation of (poly)sulfide and peroxydisulfate electrolytes has also been described.[18b,24]

Sample Composition. The composition of the graded samples was determined by Auger electron spectroscopy (AES) in conjunction with Ar. ion sputter etching. AES data were obtained on a Physical Electronics Model 548 instrument using a 3-keV, 40-μA primary electron beam which was ∿200 μm in diameter. Peaks for Cd, S, and Se at 376, 152, and 1315 eV, respectively, were monitored. Sputter etching was conducted using a ∿2 mm diameter beam of 5-keV, 25-mA Ar ions with the vacuum chamber backfilled to ∿$5x10^{-5}$ torr with Ar. The sputter rate was determined by masking part of a CdS crystal with stainless steel and sputtering over the interface; subsequently, the step height was determined on a Hacker Model H/I 700 interference microscope from the observed fringe shifts. Comparable sputtering rates for CdS and CdSe have been reported, suggesting that preferential sputtering is not significant in this system.[22] To independently obtain the graded-region width, part of the crystal was masked with nail polish and the exposed portion repetitively

etched with dilute Br_2/H_2O (1:200 v/v) while monitoring PL spectra (457.9-nm excitation in air) between etchings (vide infra). After removing the nail polish with acetone, the step height was determined on a Sloan Instrument Co. Dektak contacting stylus.

Electrical Characteristics. Four-point probe resistivity measurements were performed on a Signatone Corp. instrument. Capacitance vs. potential measurements were obtained at 1 MHz with a Boonton Electronics Model 72BD capacitance meter and a Hewlett-Packard Model 1454 variable power supply. The crystal was etched down to the substrate on one side and ohmically contacted with Ag paint to the sample holder. The opposite crystal surface was only lightly etched (Br_2/H_2O, 1:1000 v/v for 2s) and contact was made to Au dots (0.025-cm diameter) which had been vacuum-deposited with the aid of a grid on a Hitachi Ltd Type HUS-4GB Vacuum Evaporator. Measurements were made at several depths, exposed by chemical etching, and also on the CdSe substrate.

X-ray Diffraction. To examine crystallinity, an ∿10 mg CdSe sample was coarsely ground and placed in an evacuated quartz ampule with ∿30 mg S and heated in the Lindberg furnace (700°C) for 4 days. Yellowish granules were subsequently ground to a fine powder and sealed in a 0.3-mm o.d. glass tube. X-ray data were obtained with a Philips Electronic Instruments Type 12215/0 powder diffractometer equipped with a Weissenberg camera. Exposure times were 3 hrs to Ni-filtered CuK_α radiation. The patterns were measured to ±0.02 mm using a Norelco film reader and matched those of a crystalline CdS sample, obtained from Cleveland Crystals, Inc., as well as literature data.[25]

Optical Measurements and PL Properties. Uncorrected, front-surface PL spectra (200-800 nm) were obtained with the Aminco-Bowman spectrophotofluorometer, as described previously.[2b] A Coherent Radiation CR-12 Ar ion laser was used for 457.9- and 514.5-nm excitation; a CR590-03 dye laser, pumped by the Ar ion laser, was used for 580-nm excitation. Interference filters were used to eliminate laser plasma lines, and solution or glass filters were used in the emission spectrometer to eliminate laser excitation lines;[2b] the 580-nm excitation line was filtered out

using a Corning 2-60 filter. PL spectra between 750 and 1100 nm were obtained with 457.9-nm excitation using the McPherson-based spectrometer described previously.[2b] PL spectra in 5M OH^- solution were acquired using 457.9-, 514.5- and 580-nm excitation by 10X expanding and masking the 2-3 mm diameter laser beam to fill the sample surface; identical intensities (ein/s; measured with a Tektronix radiometer[2b]) at the three excitation wavelengths were used without changing the sample geometry. PL spectra resulting from excitation of different crystal strata with 457.9-nm light were obtained in air by the incremental removal of surface material through chemical etching with dilute Br_2/H_2O (1:1000 v/v). After each etching the PL spectrum was recorded in roughly the same geometry. For probing lateral inhomogeneity, the laser beam was focused to ~0.5 mm in diameter; the PL spectra resulting from 457.9-nm excitation at various sites on the crystal surface were then obtained by slight variations in the crystal-detection optics geometry.

PEC Experiments. PL properties in a PEC were acquired in 1M OH^-/1M S^{2-}/(0.1M S) (poly)sulfide electrolyte using cells and electrochemical equipment previously reported.[2b] Typically, 457.9-nm light was used for excitation and was delivered in an expanded, masked beam. PL spectra were recorded while sitting at various potentials without changing the cell geometry. The open-circuit spectra were run before and after in-circuit spectra to demonstrate reproducibility. Complete i-V curves were also obtained in this geometry. Direct measurement of ϕ_x required re-assembling the cell outside of the spectrometer, as described previously.[18b] Photoaction spectra were obtained using light from a 300-W, tungsten-halogen projector bulb; the lamp's output was monochromatized by passing the light through a McPherson Model 270, 0.35-m monochromator equipped with a grating blazed at 500 nm. Lamp intensity as a function of wavelength (460-800 nm) was measured with a flat-filtered EG & G Model 550-1 radiometer;[2b] the radiometer's output was displayed on a

Houston Model 2000 x-y recorder and converted to relative einsteins. Photocurrent from a PEC employing the graded electrode and optically transparent 1 M OH^-/1M S^{2-} electrolyte was then measured at -0.30 V vs. SCE (output displayed on the Houston recorder) and corrected for the variation in light intensity to generate the photoaction spectrum.

EL Spectra. Uncorrected EL spectra were obtained in 5M NaOH/0.1M $K_2S_2O_8$ electrolyte by pulsing the electrode between 0.00 V (6s) and a potential cathodic of ~-1.0 V (1s), while slowly scanning the emission monochromator (12 nm/min), as described previously.[2b,24]

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Figure Captions

Figure 1. Auger/depth profile analysis of an S-exchanged CdSe sample prepared as described in the text. Sputter etching employed Ar ions and was conducted at a rate of ∿300 Å/min.

Figure 2. Uncorrected PL spectra of an S-exchanged CdSe sample prepared as described in the text. All spectra were obtained in air with 457.9-nm excitation. Curve 1 is the PL spectrum of the as-grown sample and curves 2-5 are spectra obtained after successive chemical etchings with a Br_2/H_2O solution (1:1000 v/v) of 0.5,3.0,4.5 and 16 min, respectively. The ∿0.3-cm^2 exposed surface area of the sample was uniformly irradiated with ∿1.5 mW of power, and the excitation geometry was made as nearly identical as possible throughout the experiment.

Figure 3. Uncorrected PL spectra of homogeneous, single-crystal CdS_XSe_{1-X} samples irradiated in 5M OH^- electrolyte while they were held at -1.50 V vs. SCE; similar spectra are observed in air.[2b] Curves 1-5 correspond to X = 1.00, 0.74, 0.49, 0.11, and 0.00, respectively. The ∿0.25-cm^2 samples were excited with ∿1.0 mW of 457.9-nm light (excitation spike shown at 1/100 the scale of the PL spectrum). Emission intensities are not directly comparable because of differences in geometry.

Figure 4. Uncorrected EL and PL spectra of the sample of Figure 1. The series of vertical lines constitutes the EL spectrum which was obtained in 5M NaOH/0.1M $K_2S_2O_8$ electrolyte by repetitively pulsing between 0.00 V (6 s) and -1.50 V vs. SCE (1 s) while scanning the emission monochromator at 12 nm/min. PL spectra were obtained in 5M OH^- electrolyte without changing the sample geometry from that employed in the EL experiment. The ∿0.25-cm^2 exposed surface area of the sample was uniformly irradiated with ∿$6x10^{-8}$ ein/s of 457.9- (—), 514.5- (---), and 580- nm (-.-.) light.

Figure 5. Photoaction spectrum for a PEC employing an S-exchanged CdSe electrode prepared as described in the text. The electrode was held at -0.30 V vs. SCE in an optically transparent 1M OH^-/1M S^{2-} electrolyte. Plotted values of relative photocurrent have been corrected for variation in light intensity as a function of wavelength.

Figure 6. PL spectra and i-V properties of an S-exchanged CdSe sample prepared as described in the text. The inset shows i-V properties obtained with 457.9-nm excitation of the electrode when incorporated in a PEC employing a 1M OH^-/1M S^{2-}/0.1M S electrolyte. The Ar ion laser used for excitation was beam-expanded and irradiated the $\sim$0.25-cm^2 exposed sample surface area with 1.7 mW of power. A sweep rate of 10 mV/s was used and the electrolyte redox potential was -0.75 V vs. SCE. Corresponding uncorrected PL spectra obtained at open circuit and -0.30 V vs. SCE are shown as the solid and dashed curves, respectively. Both spectra were taken in identical geometries, as described in the Figure 2 caption.

Fig 1 18

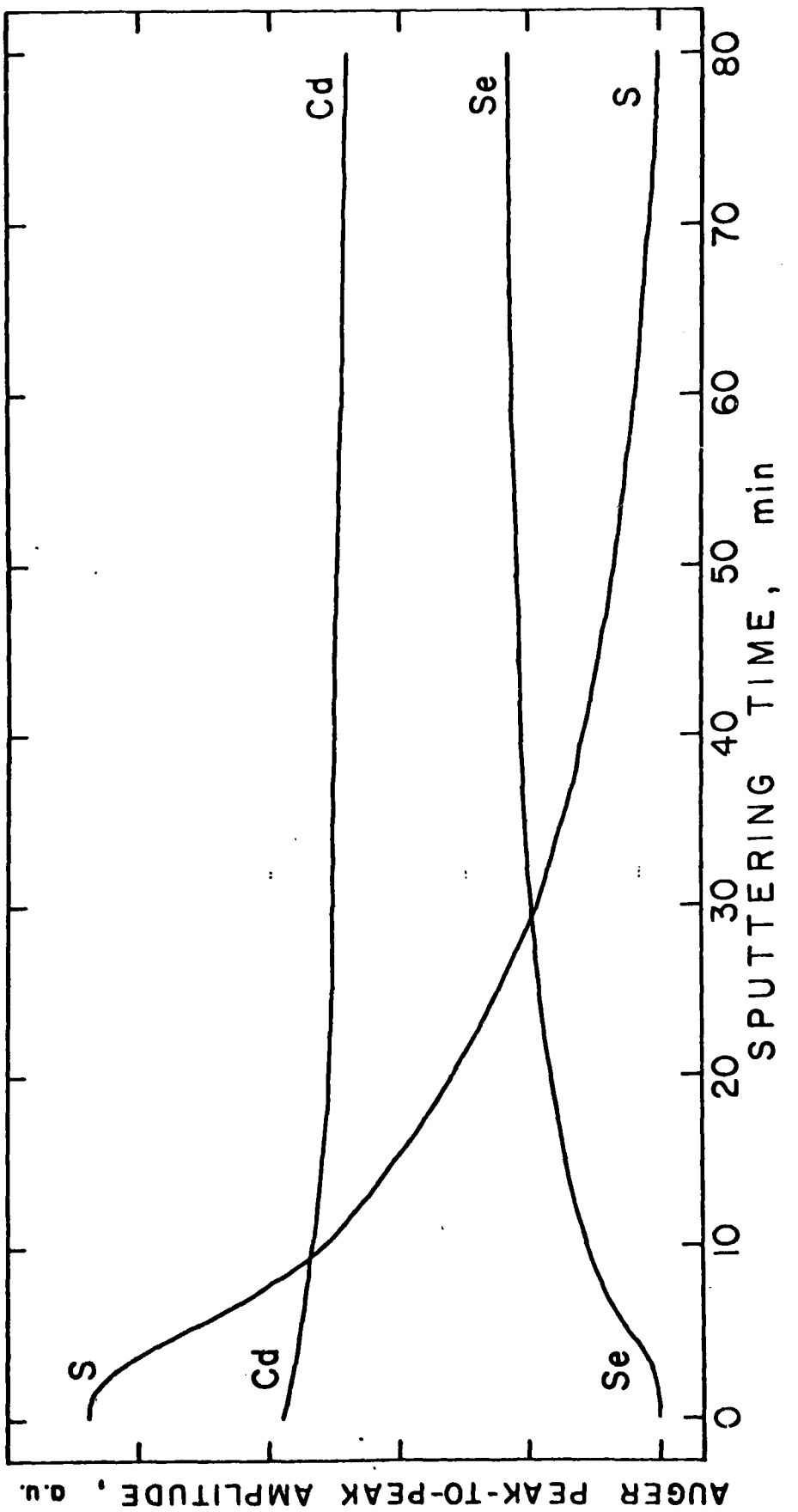

AUGER PEAK-TO-PEAK AMPLITUDE, a.u.
SPUTTERING TIME, min
0
10
20
30
40
50
60
70
80
Cd
Se
S
S
Cd
Se

Fig 2

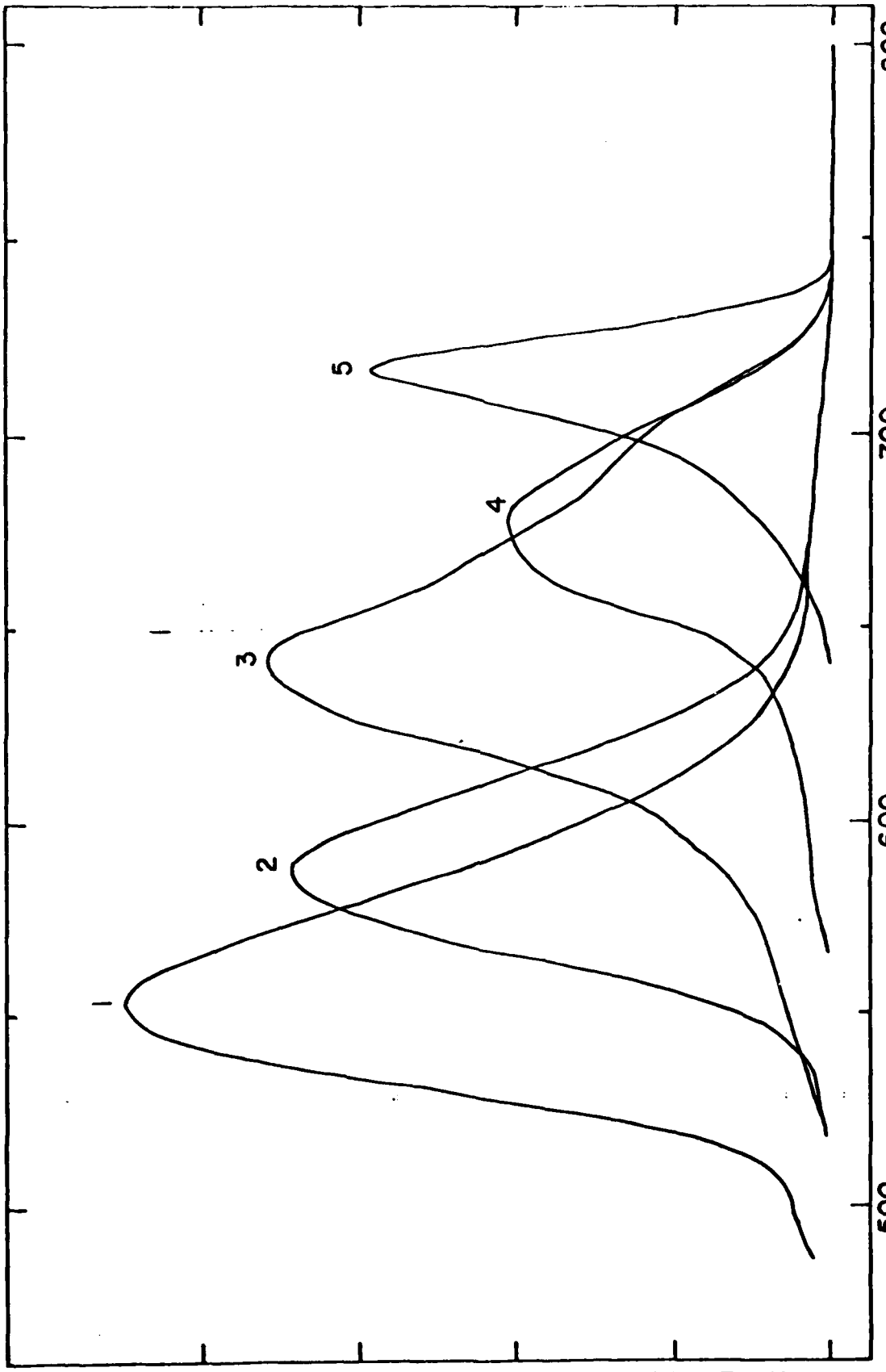
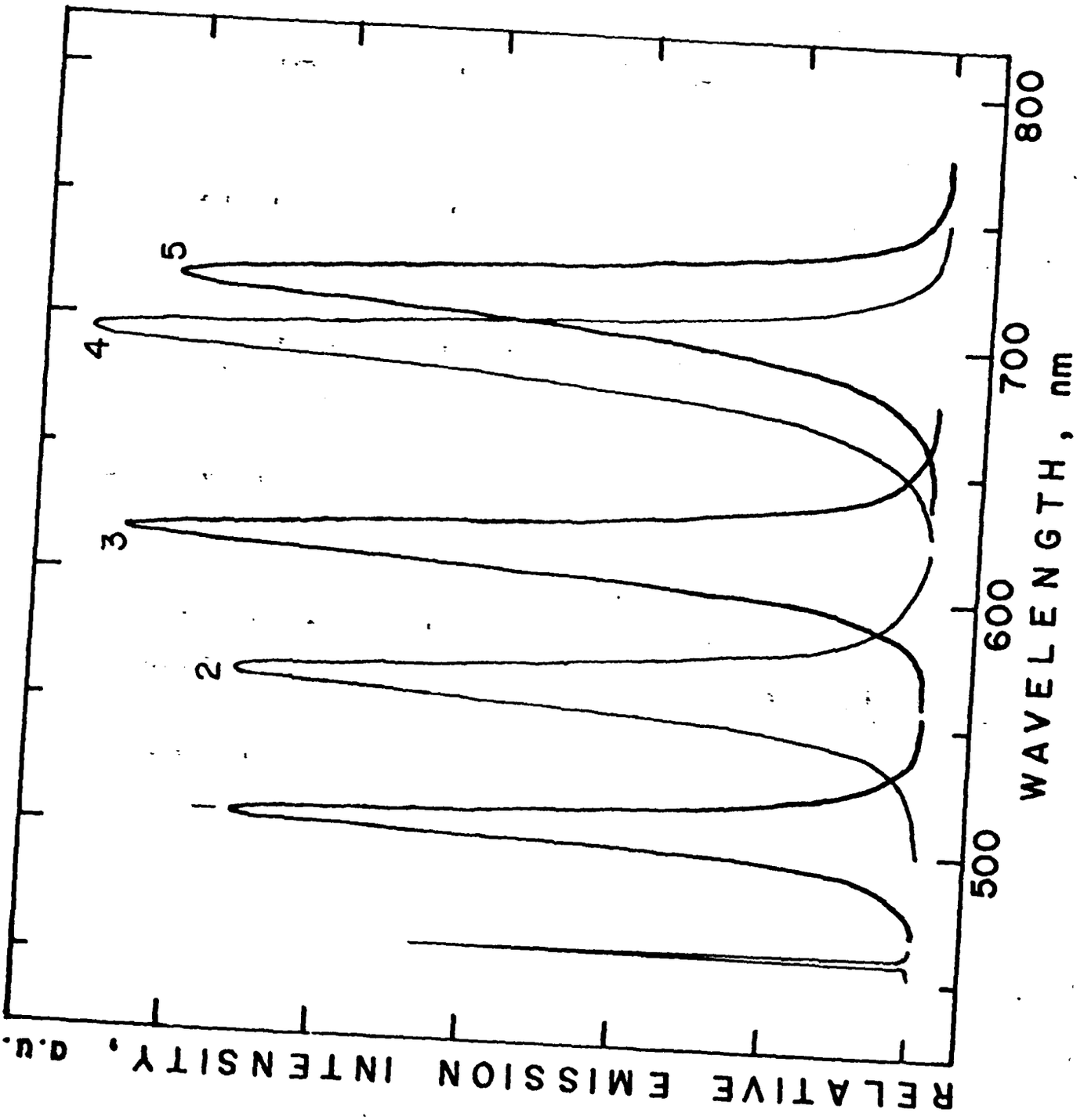

RELATIVE EMISSION INTENSITY, a.u.
WAVELENGTH, nm
500
600
700
800
1
2
3
4
5

Fig 3. 20


RELATIVE EMISSION INTENSITY, a.u.
WAVELENGTH, nm
500
600
700
800
1
2
3
4
5

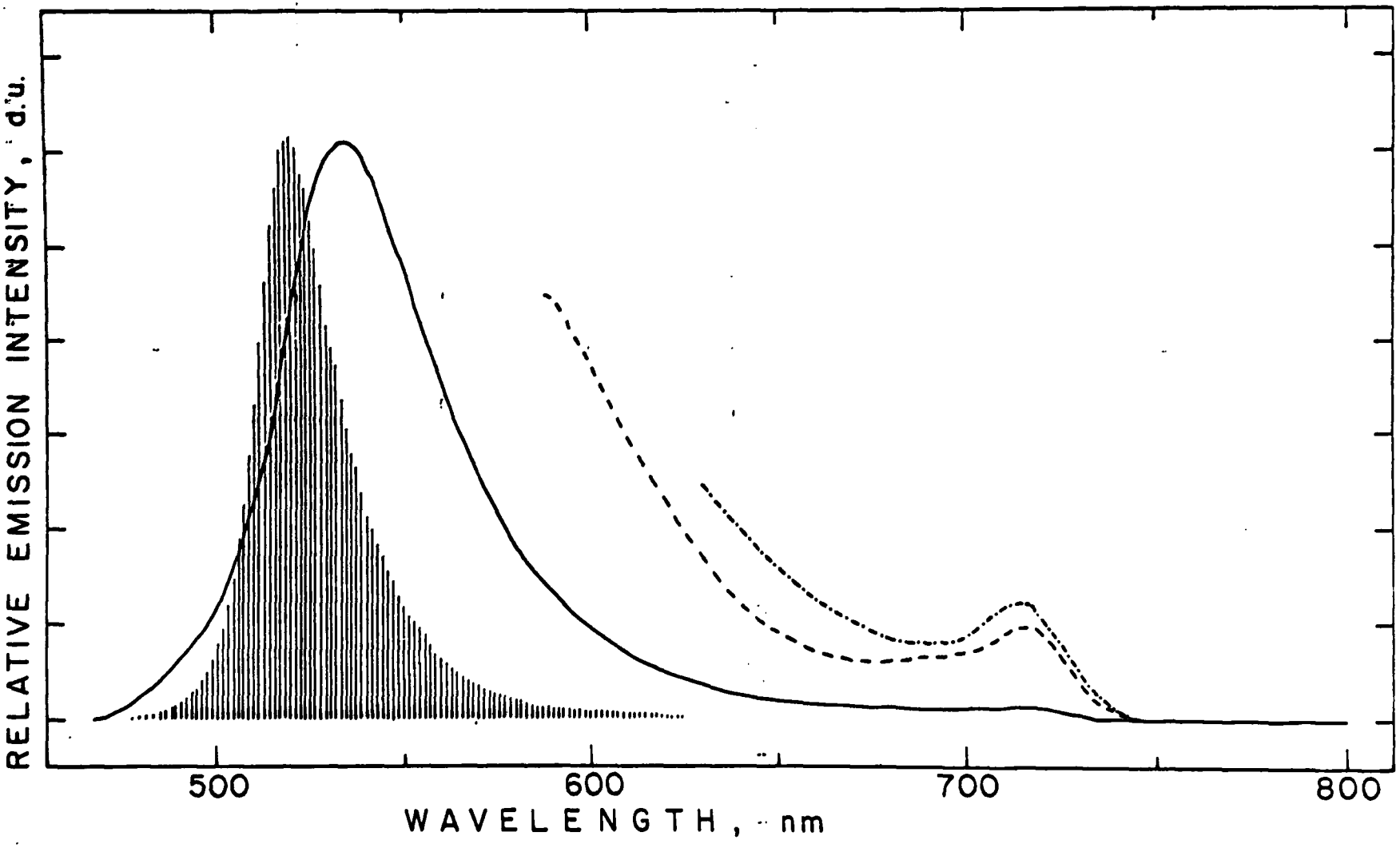

RELATIVE EMISSION INTENSITY, d.u.
500
600
700
800
WAVELENGTH, nm

Fig 4

Fig 5

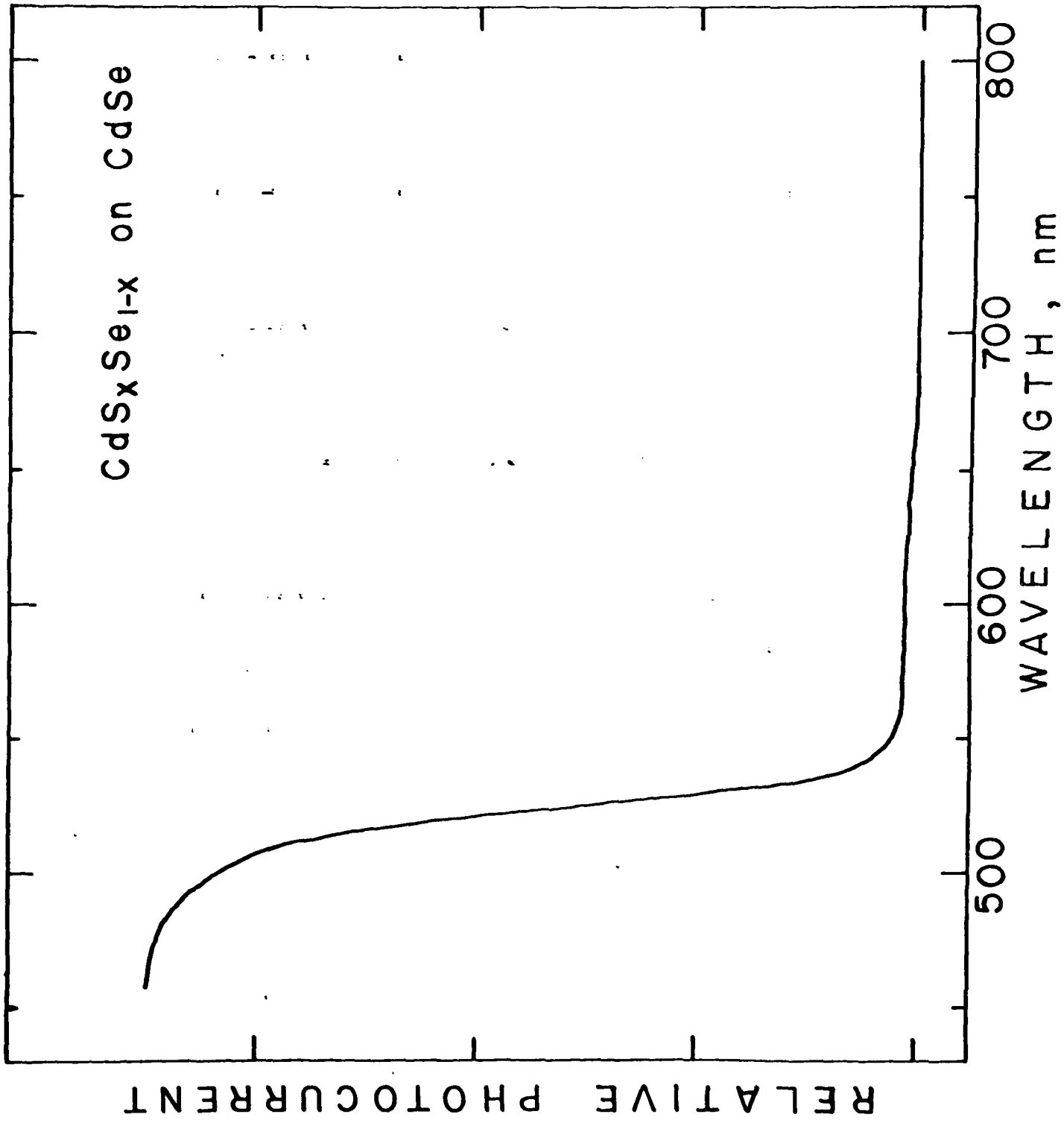
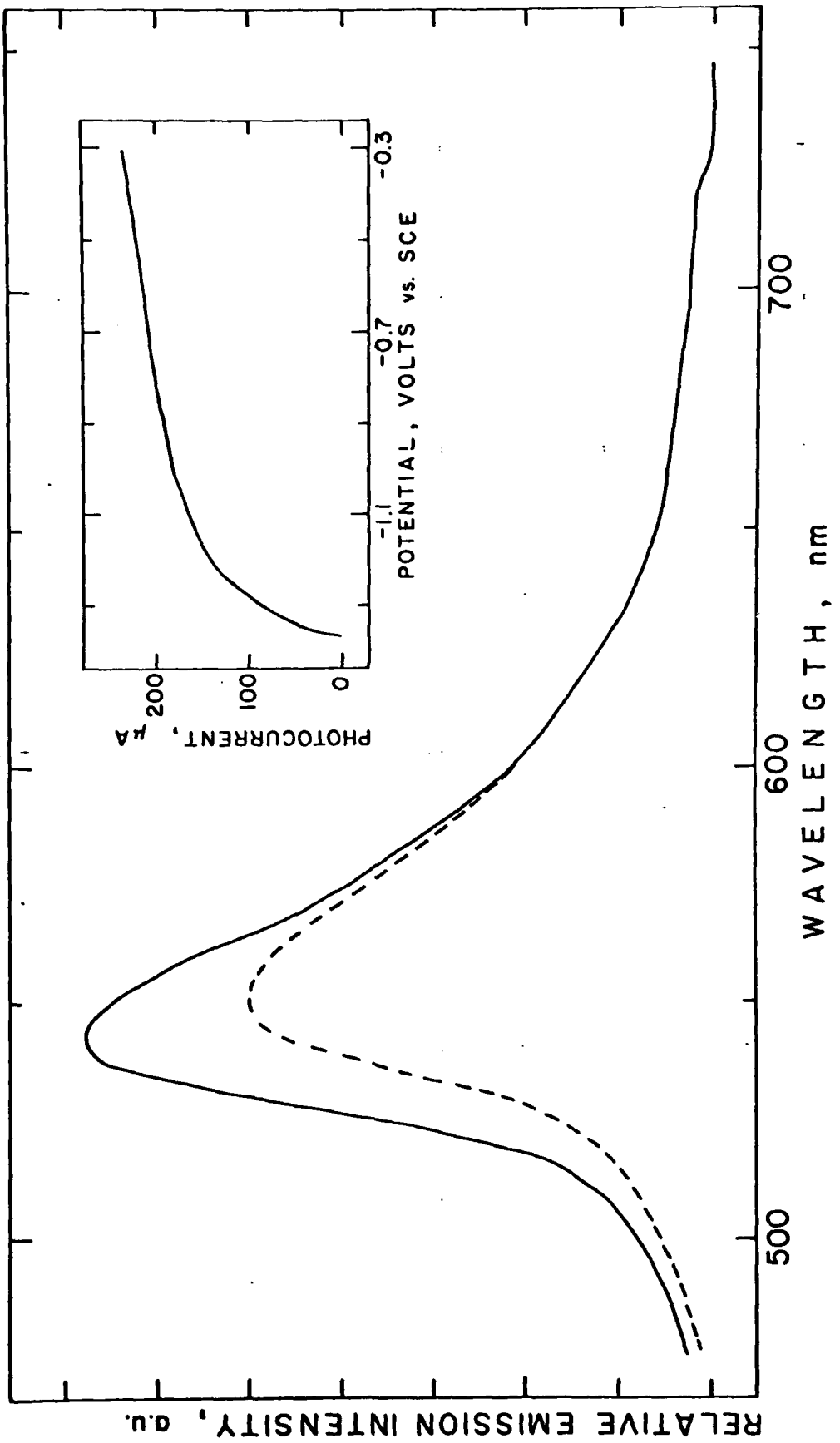

CdSxSe1-x on CdSe
RELATIVE PHOTOCURRENT
500
600
700
800
WAVELENGTH, nm

Fig 6


RELATIVE EMISSION INTENSITY, a.u.
500
600
700
WAVELENGTH, nm
PHOTOCURRENT, μA
0
100
200
-1.1
-0.7
-0.3
POTENTIAL, VOLTS vs. SCE

ATE
LME